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Catalytic solar water splitting inspired by photosynthesis. homogeneous catalysts with a Mechanical ("Machine-like") action

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Abstract

Chemical reactions may be controlled by either: the minimum threshold energy that must be overcome during collisions between reactant molecules / atoms (the Activation Energy, Ea), or: the rate at which reactant collisions occur (the Collision Frequency, A) (for reactions with low Ea). Reactions of type (2) are governed by the physical, mechanical interaction of the reactants. Such mechanical processes are unusual, but not unknown in molecular catalysts. We examine the catalytic action and macroscopic properties of several abiological mechanical catalysts and show that they display distinct similarities to enzymes in general. An abiological model of the Photosystem II Water Oxidizing Complex that appears to employ a mechanical action has now been found to be a remarkably active and sustained molecular catalyst of water oxidation when illuminated by sunlight. A free-standing Dye-Sensitized Solar Cell that spontaneously splits water into hydrogen and oxygen has been developed using this catalyst.

Keywords

mechanical, machine, like, homogeneous, action, photosynthesis, inspired, splitting, water, solar, catalytic, catalysts

Disciplines

Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences

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Catalytic Solar Water Splitting Inspired by Photosynthesis. Homogeneous Catalysts with a Mechanical (“Machine-Like”) Action

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INTELLIGENT POLYMER
RESEARCH INSTITUTE

Sub-theme: Molecular Machines

- Much interest in developing "*molecular machines*" that drive chemical reactions

- But, what is the "*mechanical action*" that must occur within a molecular catalyst to turn it into a *molecular machine*?

Two General Methods of Inducing Change

- **Energy Gradient ("*Thermodynamics*")**

  Change driven by an overall <u>release of energy</u>

  e.g. a ball falling to Earth under gravity

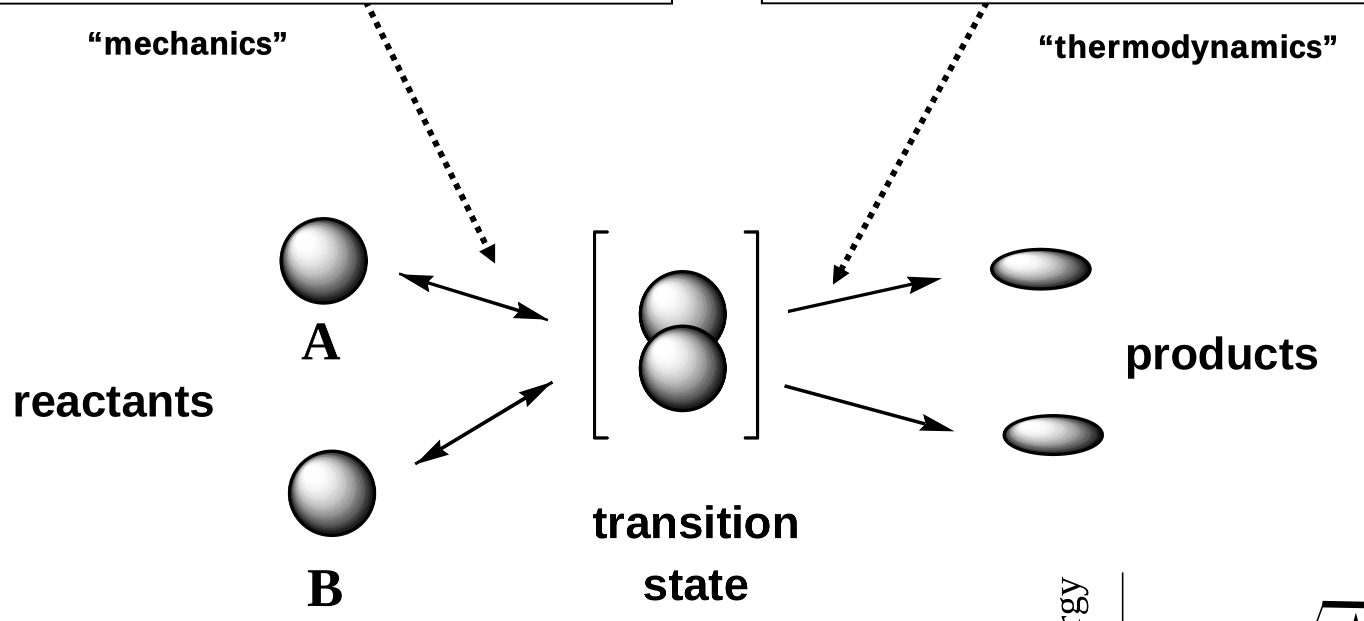
- **Mechanical Interaction ("*Mechanics*")**

  Change driven by a physical <u>collision</u> (action-reaction sequence that plays out over time)

  e.g. two billiard balls physically colliding

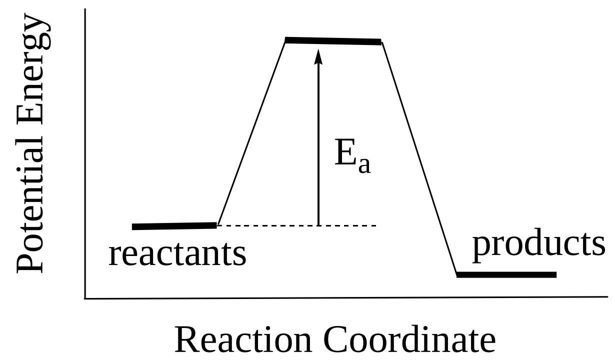
Chemistry: Collision Theory

STEP (1)	STEP (2)
Reactant collision controlled by the *"collision frequency" (A)*	Product formation controlled by the *"activation energy" (E_a)*



"Mechanical" reaction:

$$H^{+} \quad + \quad OH^{-} \longrightarrow H_2O \qquad k = 10^{-10}\,s$$



What Happens in Catalysis?

STEP (1)

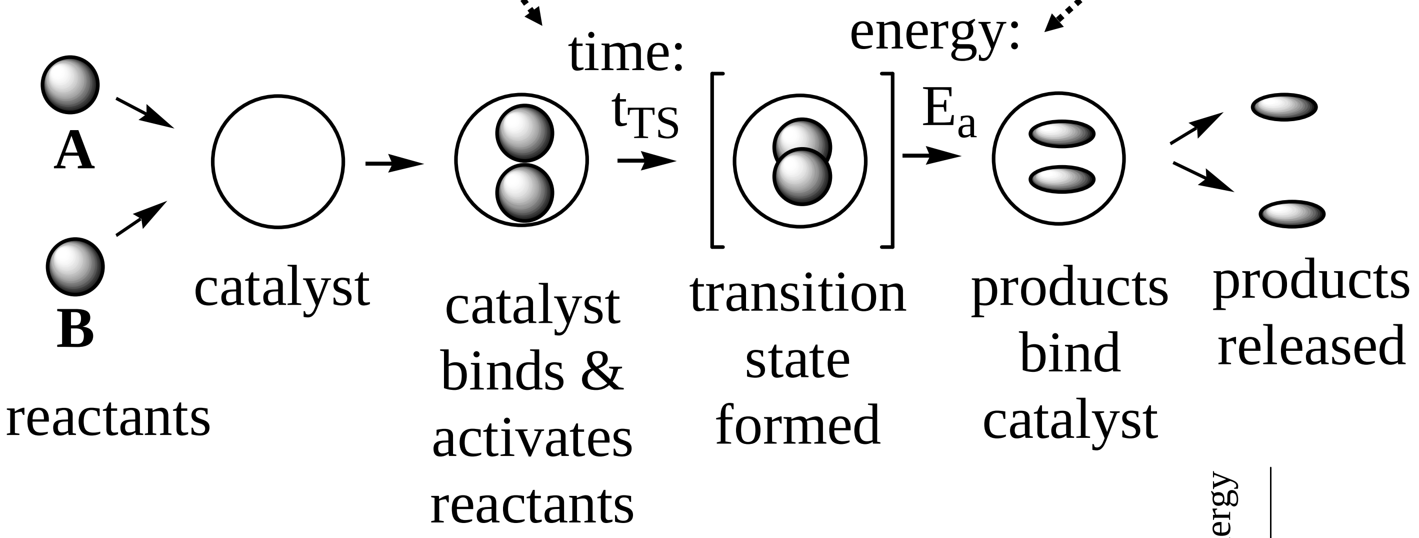
Reactant collision controlled by the *"collision frequency" (A)*

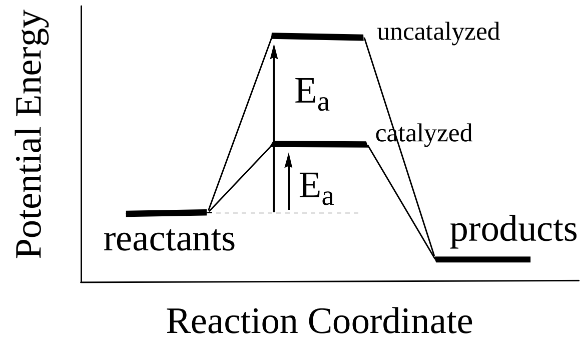
STEP (2)

Product formation controlled by the *"activation energy" (E_a)*

"mechanics"

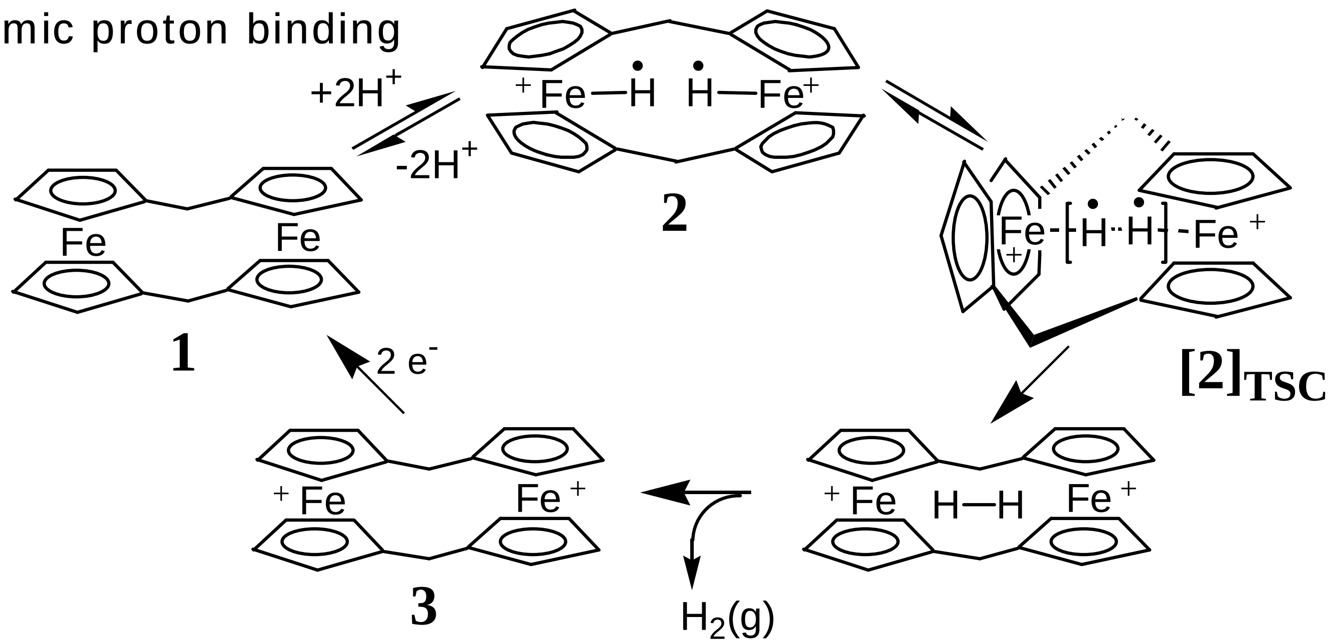
"thermodynamics"





"Mechanical" Catalysts: H_2 generation

Dynamic proton binding

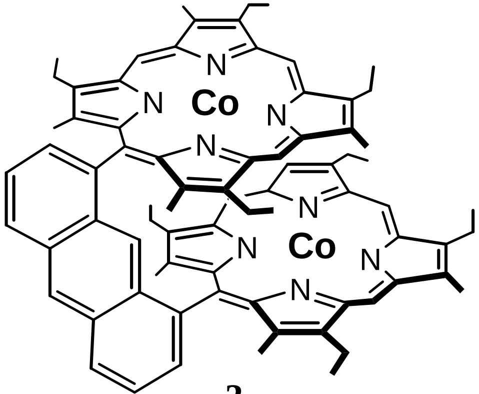


produces 5 molecules H_2 s^{-1} $catalyst^{-1}$ over at least 5 days of continuous operation

-Two dynamic processes (catalyst flexing and proton binding) which are only *synchronized* if the catalyst flexes rapidly about a structure that *complements the transition state*

Chem Commun **2004**, 308
Chem Eur J **2009**, *15*, 4746

“Mechanical” Catalysts: O_2 reduction



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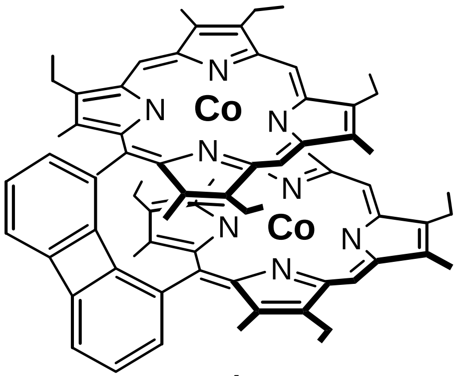

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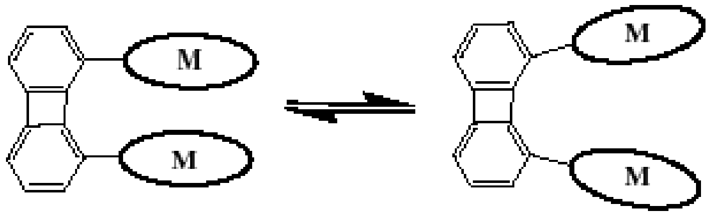
$O_2 \xrightarrow{\mathbf{3}} H_2O$ (4 e$^-$ process)

$O_2 \xrightarrow{\mathbf{4}} H_2O$ (4 e$^-$ process)



“Pac-Man” Catalyst

Chem Commun **2007**, 3352
Chem Eur J **2009**, *15*, 4746

Some Common Features of "Mechanical" Molecular Catalysts

(1) Reaction controlled by the *Catalyst-Mediated Collision Frequency* (low *Activation Energy*)

(2) The maximum catalytic rate depends on the rate of conformational flexing (conformational flexing = the "mechanical impetus")

(3) Catalyst typically flexes rapidly about a shape that *complements the transition state*

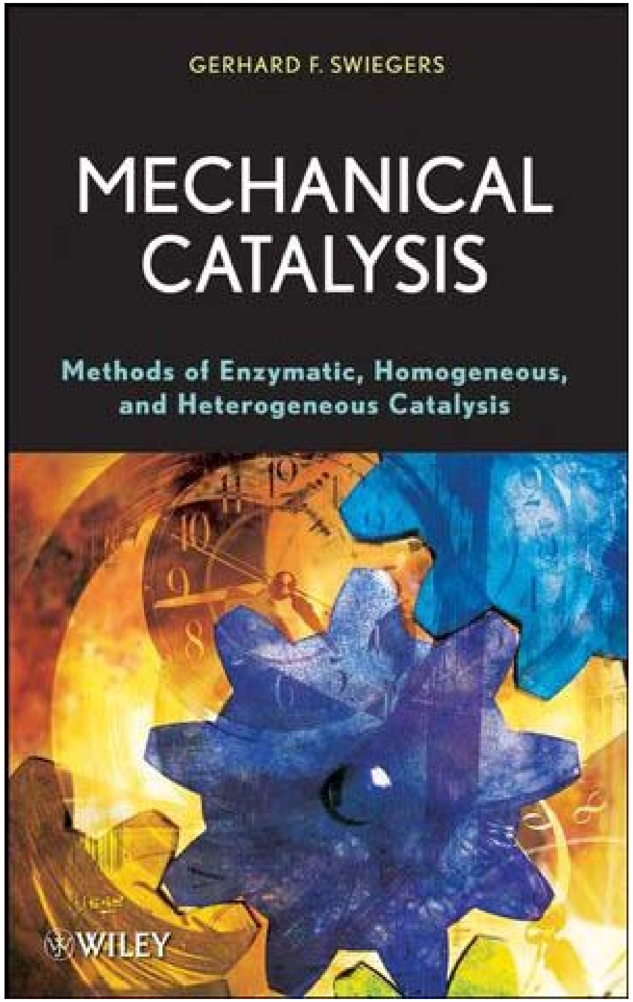
(4) Highly efficient and selective form of catalysis (like a machine)

(5) Michaelis-Menten kinetics

Chem Eur J **2009**, *15*, 4746

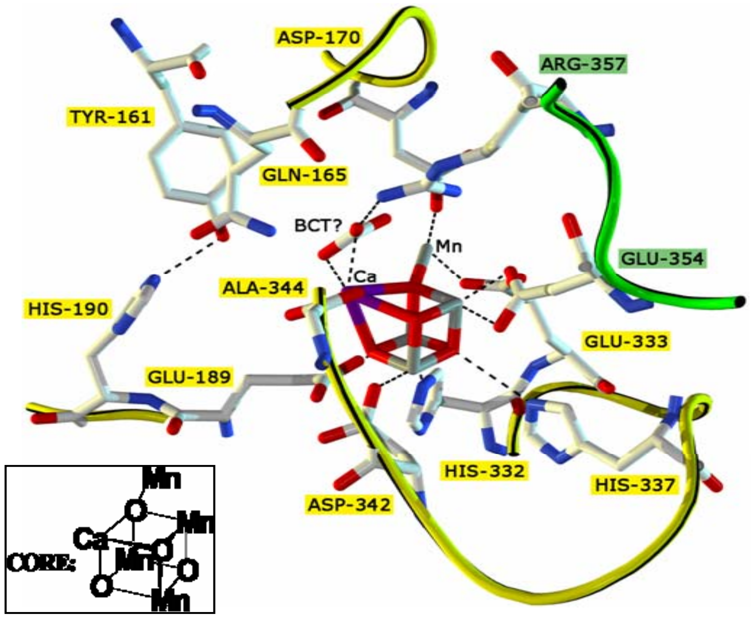
• **These features also found in many enzymes**

QUESTION: Are enzymes mechanical catalysts?



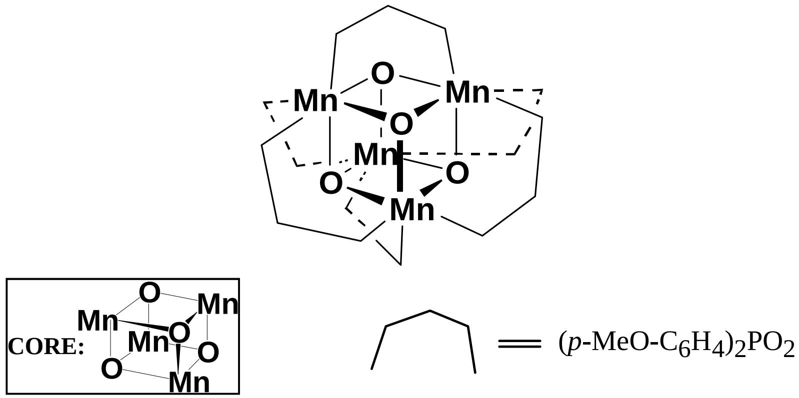
Mechanical Catalysis: Methods of Enzymatic, Homogeneous, and Heterogeneous Catalysis
Swiegers, G. F.
John Wiley & Sons, New York, 2008

Can we Mimic an Enzyme?



Water-Oxidizing Complex of Photosystem II

(PSII-WOC)

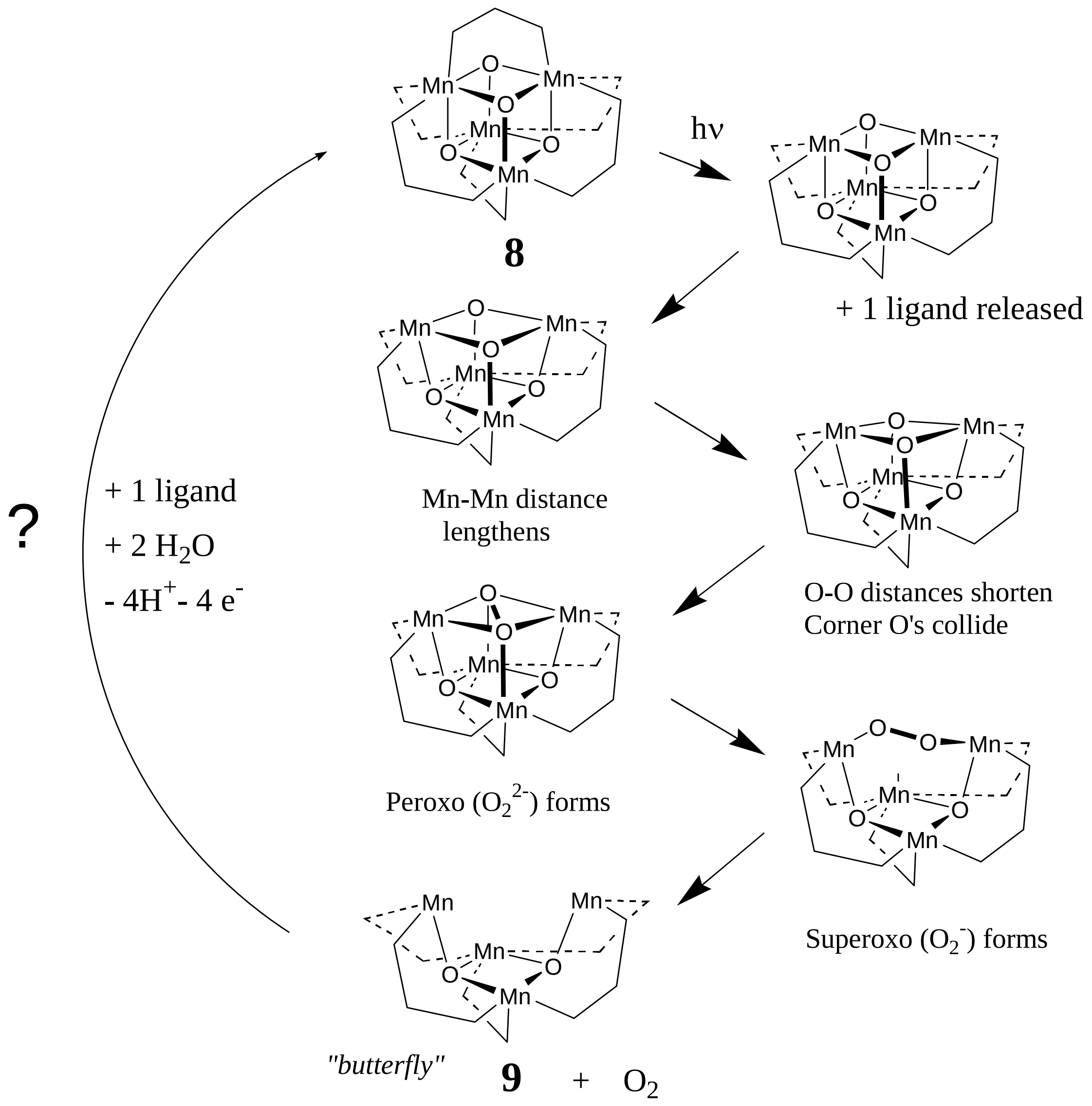


Bio-inspired Mn-oxo *Cubane* Model Complex

G. C. Dismukes, Princeton University

Cubane:
- Shape and structure similar to enzyme active site
- Dynamically self-assembles
- Flexible
- Low activation energy for O_2 release (photolytic)

Cubane forms O_2 when illuminated

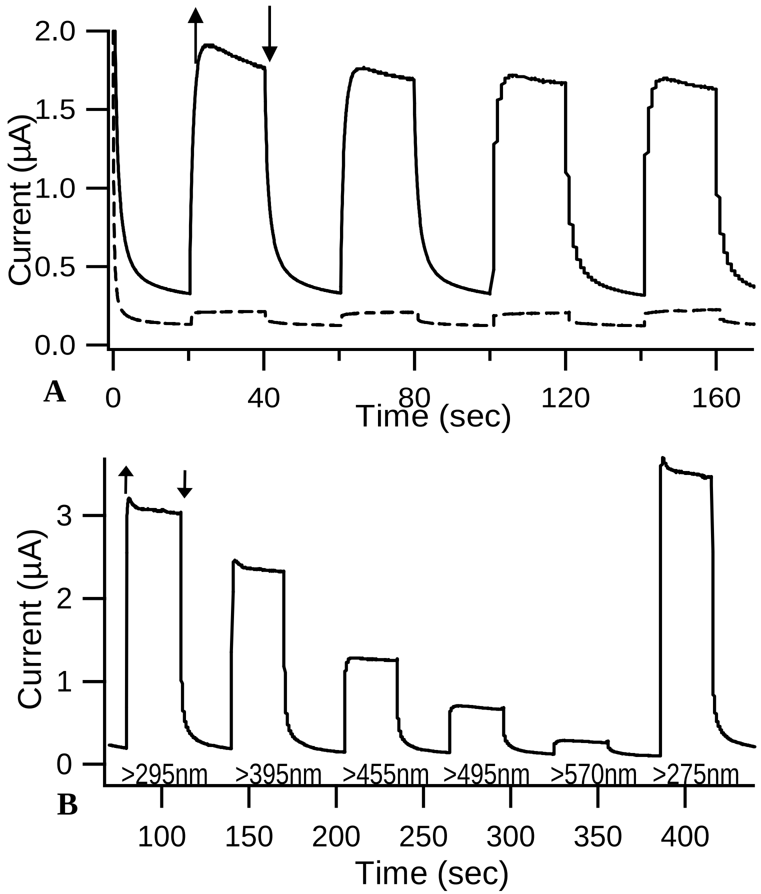


DeAngelis, Carr

Cubane in Nafion layer on GC electrode

Electrode biased at 1.0 V (vs. Ag / AgCl)

Illuminated at 250-750 nm

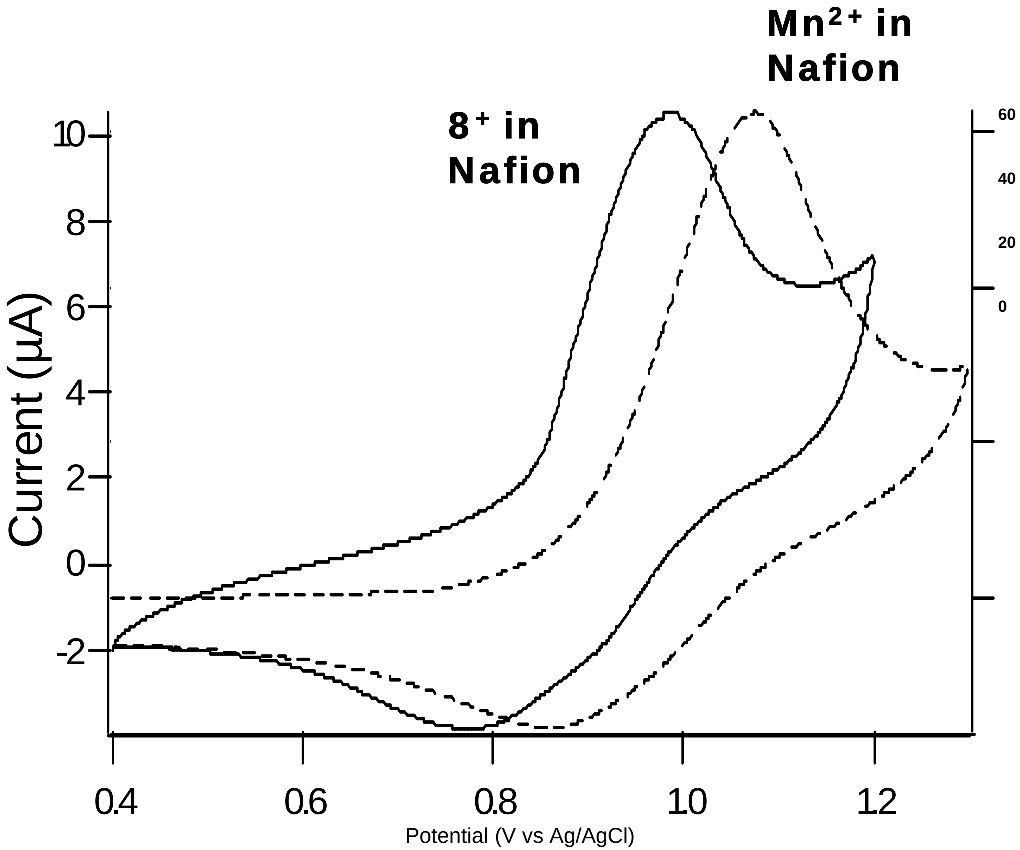


Peak turnover frequency:
270 molecules O_2 h^{-1} catalyst^{-1}

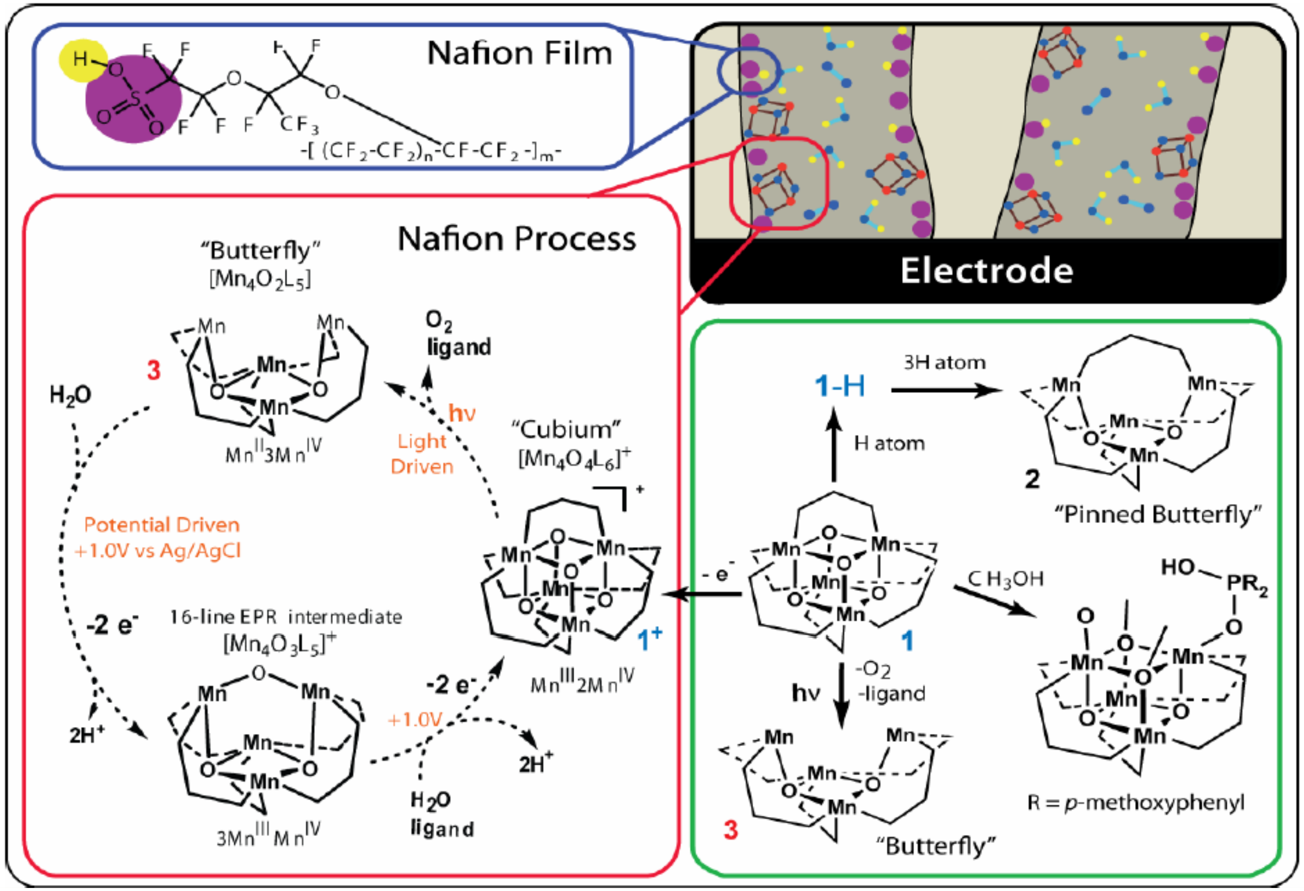
Total turnovers:
>1000 readily achieved

Angew Chem Int Ed Engl **2008**, 47, 7335

Cubane^{+} ion-exchanged into Nafion: CV



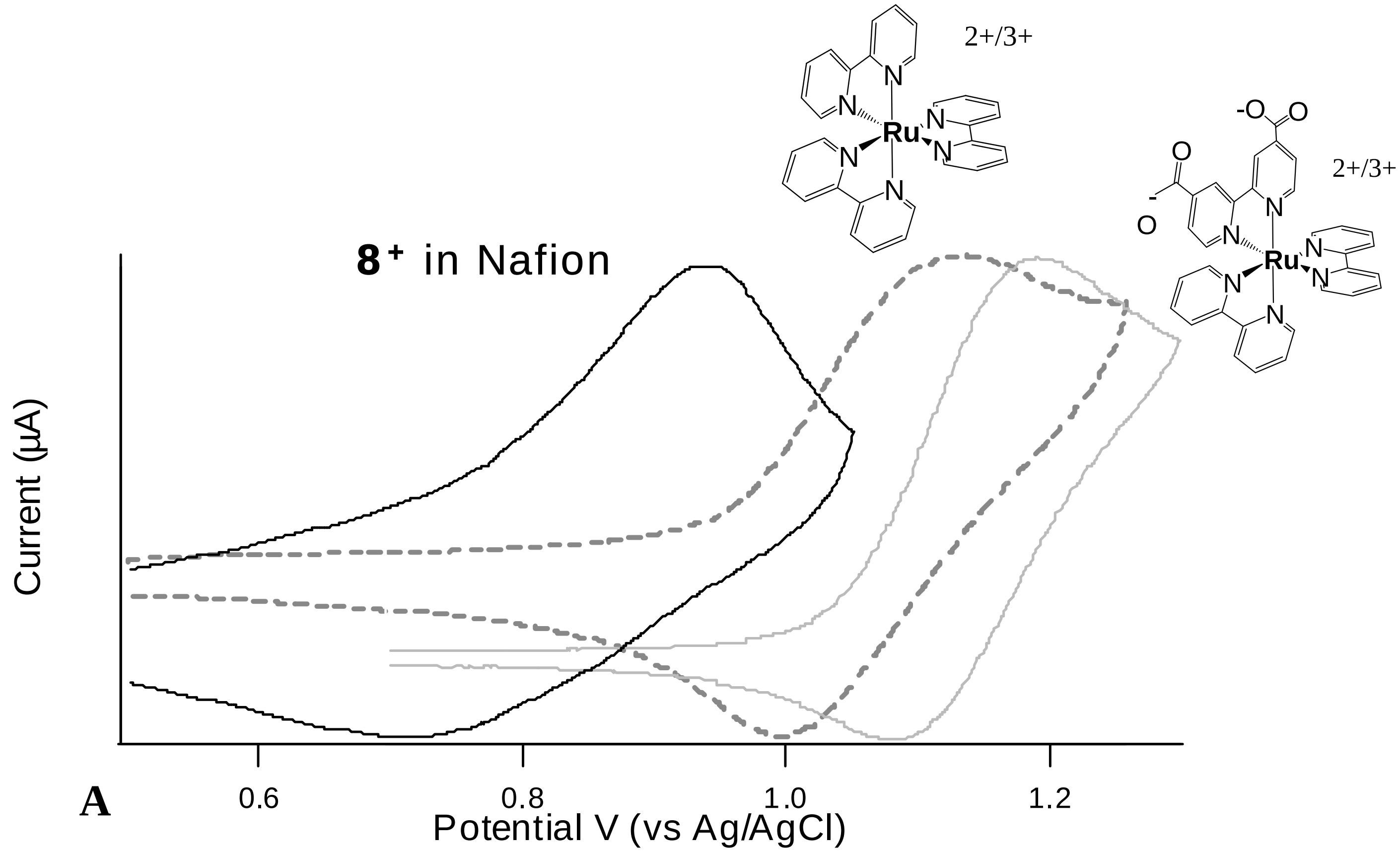
Proposed Mechanism



Catalyst dis-assembles and re-assembles under turnover conditions

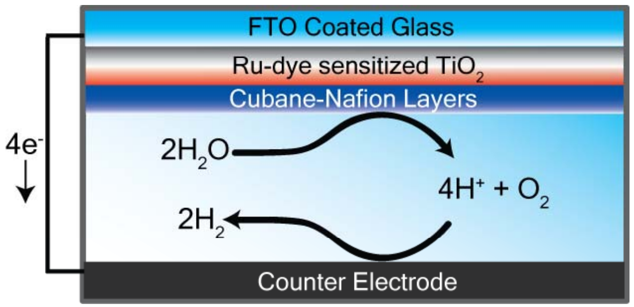
Phys Chem Chem Phys **2009**, *11*, 6441
Inorg Chem **2009**, *48*, 7269

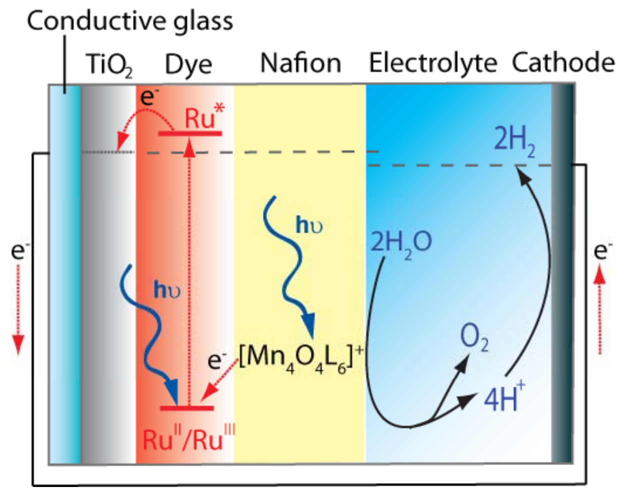
CV

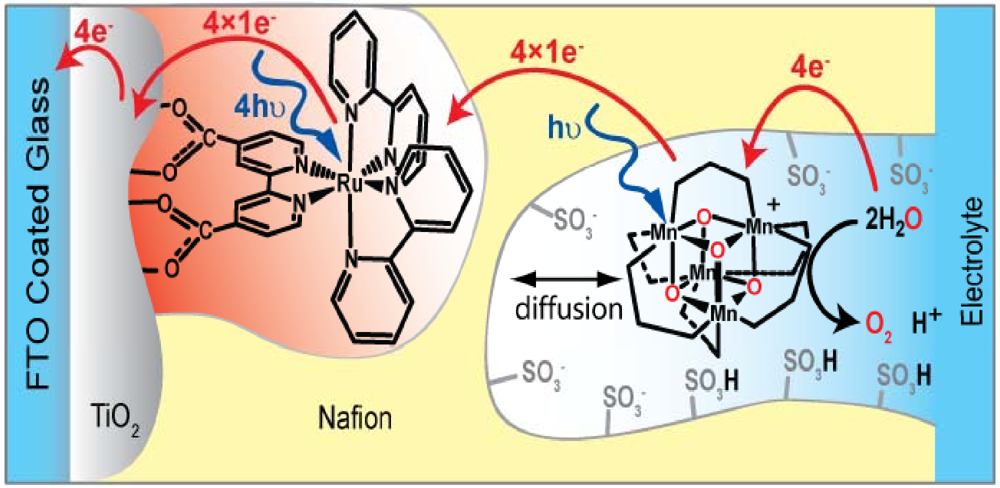


$$\mathrm{Ru(bpy)_3}^{2+} \xrightarrow{h\nu} \mathrm{Ru(bpy)_3}^{3+} + e^-$$

Water-Splitting "Graetzel" Cell

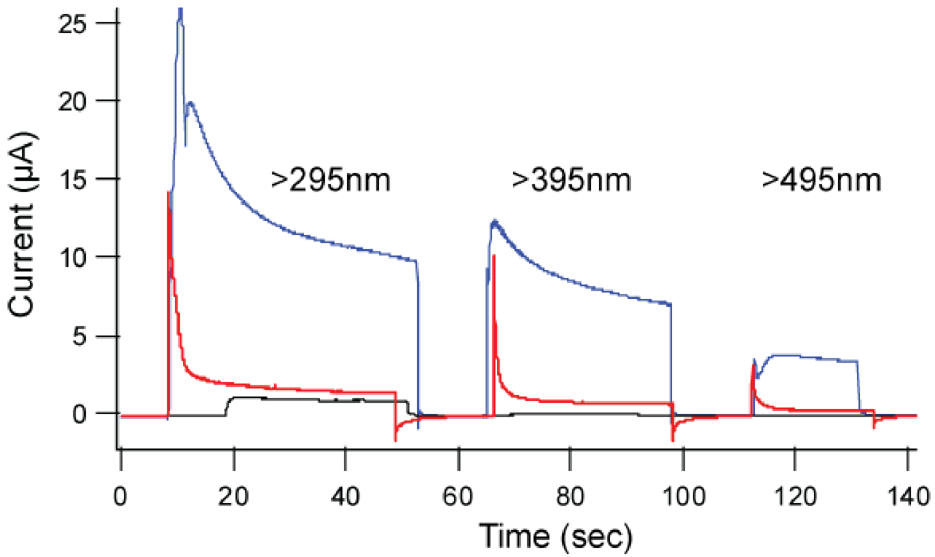


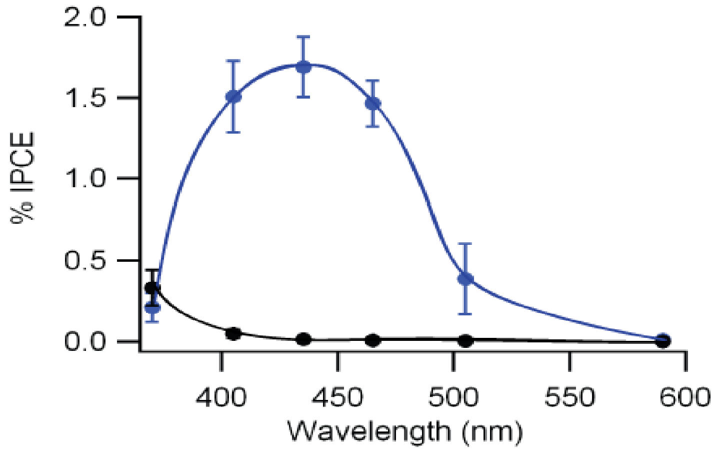




L. Spiccia, Monash University

Water-Splitting “Graetzel” Cell





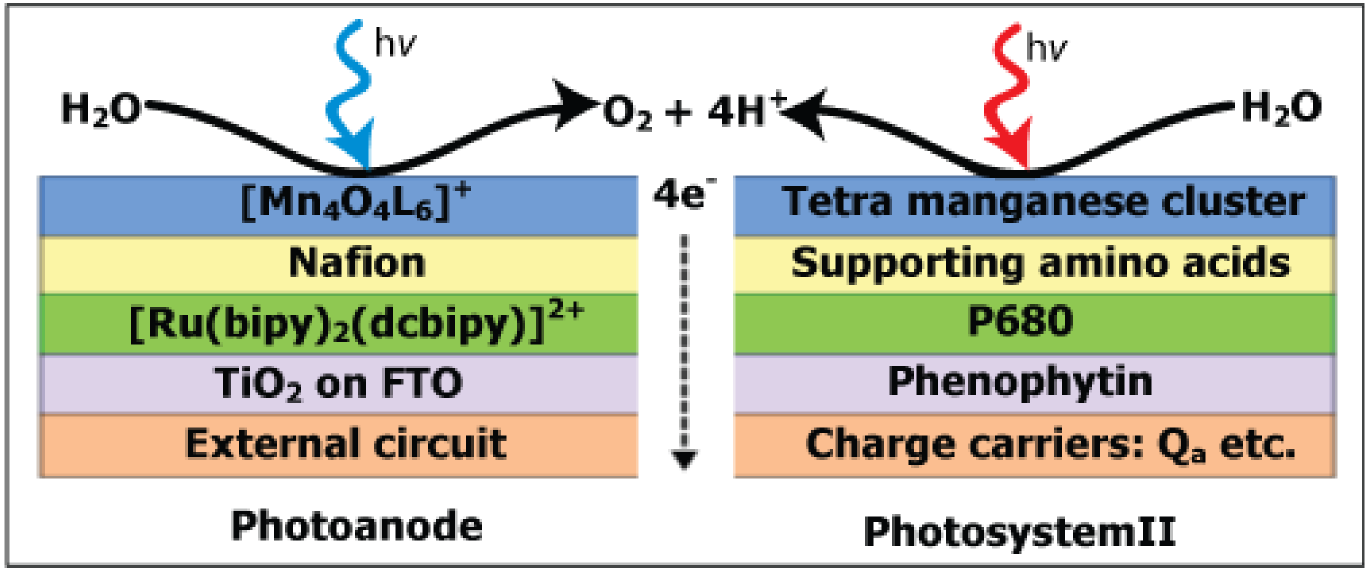
Uses H_2O as electrolyte – even impure H_2O (seawater).

Eliminates the need for acetonitrile electrolyte which bedevils existing Graetzel cells

J Am Chem Soc **2010**, 132, 2892

- **System splits seawater into pure oxygen (no chlorine formation)**
- **Spin-off company: *“Cube Catalytics LLC*”**

  (funded by New Energy Ventures, New Jersey)


hν
H2O
O2 + 4H+
hν
H2O
[Mn4O4L6]+
Nafion
[Ru(bipy)2(dcbipy)]2+
TiO2 on FTO
External circuit
4e-
Tetra manganese cluster
Supporting amino acids
P680
Phenophytin
Charge carriers: Qa etc.
Photoanode
PhotosystemII

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